

# PATENT SPECIFICATION

1,107,432

DRAWINGS ATTACHED.

Date of Application and filing Complete Specification:  
27 Aug., 1965. No. 36925/65.

Application made in United States of America (No. 393,617) on  
1 Sept., 1964.

Complete Specification Published: 27 March, 1968.

© Crown Copyright 1968.



1,107,432

Index at Acceptance:—C5 E(7A1, 7A3, 7AY, 8A3C1, 8A3C2, 8A3Y).

Int. Cl.:—C 07 c 5/18.

## COMPLETE SPECIFICATION.

### Dehydrogenation Process.

We, THE LUMMUS COMPANY, a Corporation organised under the laws of the State of Delaware, United States of America, located and doing business at 385 Madison Avenue, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a dehydrogenation process and, more specifically, relates to a continuous catalytic, dehydrogenation process for converting paraffins to olefins and polyolefins and particularly to diolefins.

Dehydrogenation of paraffins to mono- and polyolefins is normally carried out on a cyclic basis in reactions supplied with a chromia-alumina catalyst. Reaction temperature of 1100°F.—1250°F. is maintained in known processes by periodically burning accumulated coke off of the catalyst. The cycle is complicated, runs are relatively short and reactors are expensive. Also, reaction of butadiene, for example, is limited, since high yield conditions also encourage coke formation.

The present invention is concerned with a continuous catalytic dehydrogenation process which is characterized by a substantial reduction in reactor expense over processes known to date and which is characterized further by flexibility in reaction severity.

In particular, the present process comprises preheating the reactant stream to reaction temperature, suspending the catalyst in the stream to form a dilute phase, passing the dilute phase through a reaction zone for a contact time of from about 1.5 to 4.5 seconds at a pressure of about 9 to 15 pounds per square inch absolute (psia) to produce polyolefins, and about 20 to 25 psia to pro-

duce mono-olefins, discharging reaction products, and unreacted reactants and catalyst, at about 2 to 5 psia to produce polyolefins, and about 12 to 15 psia to produce mono-olefins, quenching, recovering the catalyst for re-use, and recovering the reaction products.

It is an object of this invention, therefore, to provide a catalytic dehydrogenation process having a relatively inexpensive reactor. Another object is to provide such a process in which severe dehydrogenation conditions can be maintained for the formation of substantial yields of desired polyolefins. Still another object is to provide a dilute-phase, fluidized dehydrogenation process. A particular object is to provide an efficient and economic process for converting butane to butadiene.

Other objects of the invention will be apparent from the following description taken in conjunction with the accompanying drawing, which is an elevational view in section of a preferred embodiment. It will be recognized that the drawing is highly diagrammatic in form.

The invention is illustrated by conversion of butane to butadiene. Fresh butane is charged at a rate of about 30,600 pounds per hour through line 1 and is pumped via pump 2 to line 3 wherein it is mixed with a C<sub>4</sub> recycle charged to line 4, pumped by means of pump 5 at a rate of about 73,500 pounds per hour. The C<sub>4</sub> recycle contains approximately 70% butanes, 26% butenes and small amounts of butadiene, C<sub>3</sub> and C<sub>1</sub> hydrocarbons. The combined charge of about 104,000 pounds per hour in line 3 is at a temperature of about 100°F. when it is passed through heat exchanger 6, wherein it is heated to about 180°F. The heated charge is then passed through line 7 to heating coil 8 positioned in a furnace, indicated generally as 9, wherein it is heated to a tem-

[Price 4s. 6d.]

BEST AVAILABLE COPY

perature from about 1100°F. to about 1250°F., and preferably about 1175°F.

The charge is passed from furnace 9 through line 10 and is then divided into a plurality of parallel streams. While two such streams are shown, in the accompanying drawing, it is preferred that six such streams be used with the quantities of charge and catalyst specified in this illustration. It is to be understood, therefore, that only two of six streams are shown for convenience; however, it will be apparent to those skilled in the art that a plurality of streams such as six can be used in the same manner as the two streams described. Obviously, in small plants with low throughputs, only one stream to one reactor riser line is all that will be required.

As shown in the accompanying drawing, equal portions of the heated charge in line 10 are passed to lines 11 and 12, flow through which is controlled by valves 13 and 14, respectively. Catalyst is withdrawn from a regenerator indicated generally at 15, through lines 16 and 17 which are under control of valves 18 and 19, respectively. Thus, heated charge in lines 11 and 12 is at 1100—1250°F., and catalyst in lines 16 and 17 is at 1150—1250°F., when they are combined to form a dilute phase of catalyst in the charge in reactor lines 20 and 21, respectively. The pressure in the inlet ends of lines 20 and 21 ranges from about 9—15 psia, and preferably about 12 psia. Reactor lines

20 and 21 are each 100 feet in height with an inside diameter of 3.5 feet.

The dilute phase formed in lines 20 and 21 is passed upwardly at an average velocity of from about 80, and preferably about 40, feet per second. Average catalyst density varies from 0.4—1.50, and preferably about 0.90, pounds per cubic foot. The contact time during passage through lines 20 and 21 ranges from about 1.5 to about 4.5, and preferably about 2.1, seconds. In such passage, the reaction temperature is maintained between about 1150—1250°F. in each reactor line (20 and 21) dehydrogenation occurs, the heat of reaction being supplied by the hot catalyst.

Sequentially, butane is first dehydrogenated to butenes and the latter, in turn, are dehydrogenated to butadiene. The formation of butenes is favored by low hydrocarbon pressure, but as the hydrocarbon pressure is reduced even further to vacuum, the formation of butadiene is favored preferentially over that of butenes. A particular embodiment of this invention provides, ideally, the pressure conditions favorable to the sequential dehydrogenation reactions in subreaction zones. Thus, in the lower portion of each of these reactor lines, reaction conditions favor the formation of butenes; and in the upper portion thereof, reaction conditions similarly promote the formation of butadiene. For example, conditions of the following character are typical:

		At Bottom	At Top
70	Temperature, °F. ... ..	1225	1200
	Pressure, psia ... ..	12.0	3.0
	Vapor Velocity, ft./sec. ... ..	13.3	69.0
	Catalyst Density, #/ft <sup>3</sup> . ... ..	1.67	.33
	Total height, reactor feet ... ..	100	

Reaction products are passed from each of reactor lines 20 and 21 into two-stage cyclone separators indicated generally as 22 and 23, respectively, wherein catalyst and reaction products are separated. Pressure at the upper or product end of each of reactor lines 20 and 21 is from about 2 to about 5, and preferably about 3, psia. Thus a substantial pressure drop is maintained in lines 20 and 21 to favor production of butadiene in the upper portion or zone of each of lines 20 and 21. Gaseous reaction products are removed from cyclones 22 and 23 through lines 24 and 25, respectively, are combined in line 26, and are quenched immediately before any further treatment, so as to prevent undesired reactions from taking place.

Catalyst separated in cyclones 22 and 23 flows downwardly therein and is stripped with dry inert gas, such as nitrogen, intro-

duced into the bottom stripping sections of the cyclones from inert gas generating unit 27, line 28 and lines 29 and 30, flow through the latter being controlled with valves 31 and 32, respectively. The dry inert gas strips reaction products from the catalyst and is removed from cyclones 22 and 23 through lines 24 and 25, respectively.

Approximately 40,000 standard cubic feet per hour of inert gas serves satisfactorily as a stripping medium. Stripped catalyst is passed from cyclones 22 and 23 to stand pipes 33 and 34, respectively, each of which is about 67 feet high. A dense catalyst phase is maintained in each of the stand pipes and the pressure at the discharge end of each is from about 15 to about 20, and preferably about 19, psia. The catalyst flows downwardly through slide valves or other suitable valve means 35 and 36 positioned, respec-

tively, in pipes 33 and 34 into fluid bed regenerator 15. Air or other oxygen-containing combustion gas is supplied at about 24 psia through line 37 and blower 38 to the bottom or lower portion of regenerator 15 in order to burn off coke deposited on the catalyst, and to preheat the catalyst to a temperature between 1150°F. and 1250°F. The air is heated to a temperature of the order of 1175—1250°F., preferably 1200°F., by combustion with fuel gas, e.g.  $C_1$ — $C_2$  mixture or other suitable hydrocarbon fuel charged to regenerator 15 through line 39, before the air flows upwardly through grid 40 into catalyst bed 41. Flue gas formed by combustion of air and fuel gas and by removal of coke from the catalyst passes upwardly through regenerator 15 via a 3-stage cyclone indicated generally as 42, to exit line 43. Flue gas is then passed through a waste heat boiler 44, wherein heat can be recovered in the form of about 6000 pounds per hour of steam. From boiler 44, cooled fluid gas is passed through line 45 to a stack (not shown).

As indicated above, catalyst disengaging cyclones operate at a pressure of 2—5, and preferably about 3, psia. The combined reactor effluent in line 26 is at a pressure of about 2—3 psia and a temperature of about 1225°F. The combined effluent is quenched with a quench material introduced via line 47 under control of valve 48, and passed to quench vessel 46. In this way, approximately 102,500 pounds per hour of combined effluent at 1225°F. are quenched with about 1,500,000 pounds per hour of quench material, commonly referred to as "a quench oil", at about 230°F. The quench oil can be any suitable coolant consisting of a mixture of liquid hydrocarbons. The quench vessel (46) can contain suitable packing material such as Raschig rings or the like, or distributors (not shown) for promoting contact of the reactor effluent and quench oil.

Quenched reactor effluent is passed from a lower part of vessel 46 through line 49 to a lower part of scrubber 50 wherein it is in countercurrent contact with a quench oil or scrubbing medium introduced through lines 51 and 52. Approximately 865,000 pounds per hour of quench oil at 110°F. is introduced through line 52 and approximately 250,000 pounds per hour of oil at 100°F. is introduced through line 51. Butadiene and lighter gases are removed from scrubber 50 through overhead line 53 at a rate of about 113,000 pounds per hour to drum 54, through which it is passed at about 105°F. and about 2 psia through line 55 to compressors and recovery units (both of which are not shown). Approximately 15,200 pounds per hour of butadiene are so pro-

duced and recovered from the system as illustrated.

From scrubber 50 quench oil or scrubbing medium at about 230°F. are removed through line 56 and pump 57 at a rate of about 2,615,000 pounds per hour. From pump 57, a portion of the material is passed through line 47 and valve 48 to quench vessel 46. The other portion of the quenched oil is passed through line 58 to heat exchanger 6 whereupon the material is cooled to about 205°F. in indirect heat exchange with charge material from line 3. From heat exchanger 6, the oil flows to cooler 62, where it is cooled to about 110°F. About 865,000 pounds per hour of this cooled oil is passed through lines 63, 66 and 52 in quench tower 50. The remaining 250,000 pounds per hour are further cooled to 100°F. in cooler 67 and introduced via line 51 to the top of quench tower 50.

While the present invention has been described in terms of a conversion of butane to butadiene, it is contemplated that paraffins having 3 to 6 carbon atoms per molecule can be converted to mono-olefins having the same number of carbon atoms per molecule, by the process of the present invention, comprising preheating a stream containing the paraffin to a temperature between 1100°F. and 1250°F., and preheating a dehydrogenation catalyst to a temperature between 1150°F. and 1250°F., suspending the catalyst in the paraffin-containing stream to form a dilute phase, passing the dilute phase through a reaction zone for a contact time of from 1.5 to 4.5 seconds at an initial pressure of 20 to 25 psia, discharging the product from the reaction zone at a pressure of 12 to 15 psia, quenching, recovering the catalyst for re-use, and recovering the reaction products. Representative of other paraffins suitable as charge stock for the process are propane, isobutane and 2-methylbutane (isopentane).

As shown in the illustration, the hydrocarbon charge comprises a mixture of about 2.5 parts by weight of recycle for 1 part by weight of fresh feed. It is to be understood, however, that this relationship can be varied widely, with preference being given to weight ratios of 0.9:1 to 3:1.

In preheating of the hydrocarbon charge, it is desirable to heat the charge up to about the reaction temperature or to within the reaction temperature range.

Catalysts useful herein have been illustrated by a particularly preferred catalyst comprising chromia deposited upon alumina, the composition of which is about 18% by weight of chromia and the balance substantially alumina. While this is preferred, other catalysts known for their capacity to aid in the dehydrogenation of hydrocarbons, and particularly paraffins, can be employed. Representative of such materials are: metals

such as nickel, iron, cobalt, platinum and palladium; oxides of metals of Groups IVA, VA and VIA of Mendeleeff's Periodic Table, particularly chromium, molybdenum and tungsten oxides deposited upon relatively inert supports typical of which is alumina. Care should be taken with such catalysts lest they be used at excessively high temperatures at which their activity is materially reduced. Thus, in the dehydrogenation reaction and during regeneration, temperatures below the deactivation temperature characteristic of an individual catalyst are employed. For example, the preferred chromia-alumina catalyst is subjected to temperatures no higher than about 1350°F.

In the transfer reactor lines illustrated by 20 and 21 in the accompanying drawing, a dilute phase of catalyst in hydrocarbon is maintained. Generally, this phase will contain from about 20 to about 50 pounds of catalyst per pound of hydrocarbon, preferably 35 to 45.

While the invention has been described in detail according to preferred processes and preferred conditions therefor, it will be obvious to those skilled in the art that changes and modifications can be made in the details, steps, materials and arrangements of parts, without departing from the scope of the invention, and it is intended in the appended claims to cover such changes and modifications.

#### WHAT WE CLAIM IS:—

1. A process for converting butane to butadiene, which comprises:

preheating a butane-containing stream to a temperature between 1100°F. and 1250°F.;

suspending a dehydrogenation catalyst preheated to a temperature between 1150°F. and 1250°F. in said preheated butane stream to form a dilute phase of said catalyst in said stream;

passing said dilute phase through a reaction zone for a contact time of from 1.5 to 4.5 seconds at a temperature between 1150°F. and 1250°F. and at an initial pressure of from 9 to 15 pounds per square inch absolute, whereupon butane is dehydrogenated to butadiene;

discharging the resulting vaporous products containing butadiene and suspended catalyst from said reaction zone at a pressure of from 2 to 5 pounds per square inch absolute;

continuously withdrawing spent catalyst; and quenching and withdrawing said vapor products containing butadiene.

2. The process as defined in claim 1, wherein said dilute phase is passed upwardly through said reaction zone and is discharged from an upper portion of said zone.

3. The process as defined in Claim 1

or 2, wherein the catalyst density maintained in said reaction zone is between 0.4 and 1.50 pounds per cubic foot.

4. The process as defined in any of the preceding claims, wherein the butane-containing stream comprises n-butane and butenes.

5. The process as defined in any of the preceding claims, wherein the dehydrogenation catalyst comprises an association of chromia and alumina comprising about 18 percent by weight of chromia and about 82 percent by weight of alumina.

6. The process as defined in any of the preceding claims, wherein the spent catalyst is regenerated with oxygen-containing gas, reheated to a temperature between 1150°F. and 1250°F. and is recycled for suspension in said preheated butane stream.

7. The process as defined in any of the preceding claims, wherein butadiene is recovered from said quenched vapor products.

8. The process as defined in any of the preceding claims, wherein a plurality of preheated butane-containing streams and a plurality of dilute phases of catalyst in the change thereof are formed, vaporous products are combined and are quenched.

9. A process for converting butane to butadiene which comprises:

preheating a butane-containing stream to a temperature between 1100°F. and 1250°F.;

suspending a dehydrogenation catalyst preheated to a temperature between 1150°F. and 1250°F. in the preheated butane stream to form a dilute phase of said catalyst in said stream;

passing said dilute phase upwardly through a first subreaction zone at a temperature between 1150°F. and 1250°F. and at an initial pressure of from 9 to 15 pounds per square inch absolute, whereupon butane is preferentially dehydrogenated to a butene;

passing directly and upwardly from said first subreaction zone to and upwardly through a second subreaction zone the resulting dilute phase at a temperature between 1150°F. and 1250°F. and at an initial pressure of from 6 to 10 pounds per square inch absolute, the combined contact times in the two subreaction zones being from 1.5 to 4.5 seconds, whereupon said butene is preferentially dehydrogenated to butadiene;

discharging the resulting vaporous products containing butadiene and suspended catalyst from an upper portion of the latter subreaction zone at a pressure of from 2 to 5 pounds per square inch absolute;

continuously withdrawing spent catalyst; quenching and withdrawing said vapor products containing butadiene; and

recovering butadiene from said quenched vapor products.

10. A process for converting a paraffin having from 3 to 6 carbon atoms per molecule to a monoolefin having the same number of carbon atoms per molecule, which comprises:

5 preheating a stream containing said paraffin to a temperature between 1100°F. and 1250°F.;

10 suspending a dehydrogenation catalyst preheated to a temperature between 1150°F. and 1250°F. in said preheated paraffin stream to form a dilute phase of said catalyst in said stream;

15 passing said dilute phase through a dehydrogenation zone for a contact time of from 1.5 to 4.0 seconds at a temperature between 1100°F. and 1200°F. and at an initial pressure of from 20 to 25 pounds per square inch absolute, whereupon said paraffin is dehydrogenated to said olefin;

20 discharging the resulting vaporous products containing said olefin and suspended catalyst from said reaction zone at a pressure of from 12 to 15 pounds per square inch absolute;

25 continuously withdrawing spent catalyst; and quenching and withdrawing said vapor products containing said olefin.

30 11. A process for converting a paraffin having from 4 to 6 carbon atoms per molecule and having at least 4 carbons in a straight chain relationship, to a diolefin having the same number of carbon atoms per molecule, which comprises:

35 preheating a stream containing said paraffin to a temperature between 1100°F. and 1250°F.;

40 suspending a dehydrogenation catalyst preheated to a temperature between 1150°F. and 1250°F. in said preheated paraffin stream to form a dilute phase of said catalyst in said stream;

50 passing said dilute phase upwardly through a first subreaction zone at a temperature between 1125°F. and 1200°F. and at an initial pressure of from 9 to 15 pounds per square inch absolute, whereupon said paraffin is preferentially dehydrogenated to a monoolefin having the same number of carbon atoms per molecule;

55 passing directly and upwardly from said first subreaction zone to and upwardly through a second subreaction zone the resulting dilute phase at a temperature between 1100°F. and 1200°F. and at an initial pressure of from 6 to 10 pounds per square inch absolute, the combined contact times in the two subreaction zones being from 1.5 to 4.5 seconds, whereupon said monoolefin is preferentially dehydrogenated to said diolefin;

60 discharging the resulting vaporous products containing said diolefin and suspended catalyst from an upper portion of the latter subreaction zone at a pressure of from 2 to 5 pounds per square inch absolute;

65 continuously withdrawing spent catalyst; and quenching and withdrawing said vapor products containing said diolefin.

70 12. Process for converting butane to butadiene, substantially as described above with reference to the accompanying drawing.

80 13. Butadiene or another unsaturated-hydrocarbon product made by a process according to any of the preceding claims.

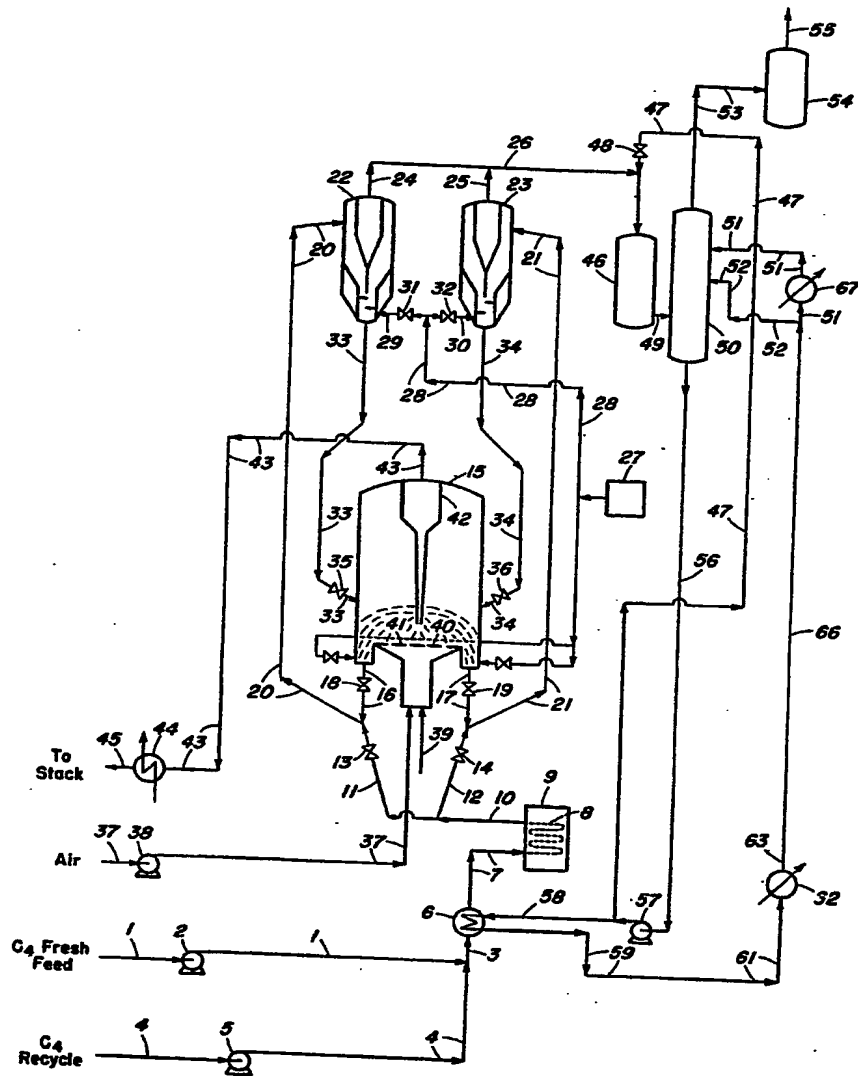
For the Applicants,  
CARPMAELS & RANSFORD,  
Chartered Patent Agents,  
24 Southampton Buildings,  
Chancery Lane,  
London, W.C.2.

1107432

COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of  
the Original on a reduced scale



BEST AVAILABLE COPY